

Biindenyls, Biindenylides, and Diindeno-Fused Heterocycles from Oxidative Coupling of 1- and 2-Indanone

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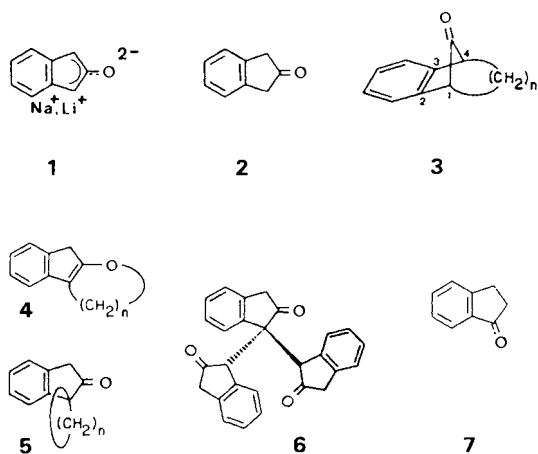
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1- and 2-indanone are transformed into the corresponding enolates and oxidatively coupled to yield 1,4-diketones providing easy access to a series of biindenyls, diindeno-fused heterocycles, and biindenylides.

Biindenyle, Biindenylide und Diindeno-kondensierte Heterocyclen durch oxidative Kupplung von 1- und 2-Indanon

1- und 2-Indanon werden in die Enolate übergeführt und oxidativ zu 1,4-Diketonen gekuppelt. Diese bieten einen einfachen Zugang zu einer Reihe von Biindenylen, Diindeno-kondensierten Heterocyclen und Biindenyliden.

We have recently demonstrated the synthetic utility of the dianion **1**, obtained by twofold deprotonation of 2-indanone (**2**) with sodium hydride and butyllithium¹⁾. Alkylation of the intermediate **1** with bifunctional electrophiles, e.g. 1,*n*-dihaloalkanes, gives three different cycloannellation products: bicyclic ketones **3** formed by attack at C-1 and C-3, bicyclic ethers **4** formed by ring formation at carbon and oxygen of **1** followed by proton migration, and the spirocyclic derivatives **5** formed by the sequence alkylation at C-1, proton transfer, and a second alkylation at C-1.



The selectivity of the process can be controlled by the chain length of the electrophile, its leaving group, and the ion-pair structure of the carbanionic intermediate. With certain electrophiles such as 1,2-dibromo-1,2-dihydrobenzocyclobutene, the alkylation of **1** is accompanied by an electron transfer to yield the "trimeric" coupling product **6**. This finding prompted us to investigate the oxidative coupling of ketone enolates derived from **2** and from the isomeric 1-indanone (**7**). The successful dehydromerization of **2** and **7** provides ready access to the hitherto unknown 1,4-diketones **18** and **13**, which are useful synthetic precursors.

1. Results

Treatment of both 2-¹⁾ and 1-indanone with sodium hydride in tetrahydrofuran (THF) at room temperature resulted in their quantitative conversion to the respective enolates **17** and **9**, which could be characterized by ¹H- and ¹³C-NMR spectroscopy (see Discussion).

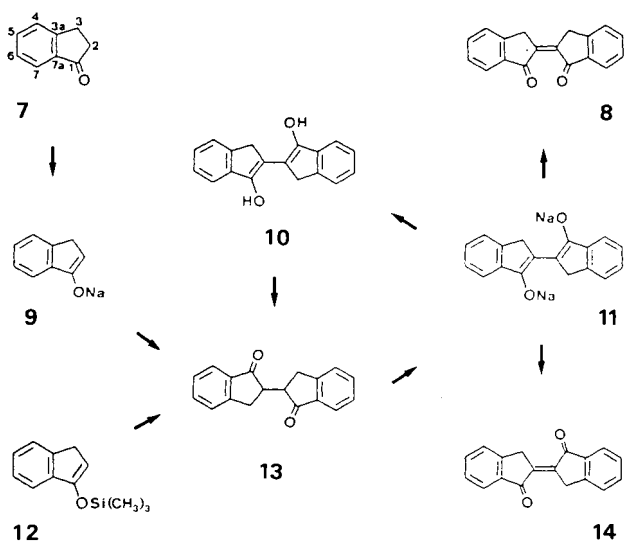
Oxidation of **9** with Cu(II) chloride in THF according to the method of Saegusa²⁾ (see Scheme 1a) afforded the dimer **13** (*meso*- and *d,l*-isomers) as only product in 50% yield, separated from the starting compound by crystallization. Depending on the experimental conditions, **13** was accompanied by varying amounts of the starting compound **7**. The related diketone **18** (*meso*, *d,l*) was obtained from **17** in only 30% yield after purification by column chromatography (see Scheme 1b). This yield was only achieved by inverse addition and the use of Cu(II) triflate instead of the chloride³⁾. The two diastereomers were separable by fractional crystallization from methanol. In order to distinguish between the *meso*- and the *d,l*-isomers of **18**, we performed ¹H-NMR measurements with shift reagents in a CDCl₃ solution of the diastereomeric mixture⁴⁾.

The main products upon oxidation of **17** with Cu(II) chloride were oligomeric polyketones, which according to their NMR, UV, IR, and FAB mass spectra have the chain structure **19**, in which partial dehydrogenation across the C-1/C-1' bonds has occurred.

As an alternative method for the linkage of two 1-indanone moieties at the 2-positions, we investigated the oxidative coupling of the readily available trimethylsilyl enol ether **12**⁵⁾ (obtained from **7** in 88% yield). Reaction of **12** with lead tetraacetate led to the formation of the desired 1,4-diketone **13** in 32% yield.

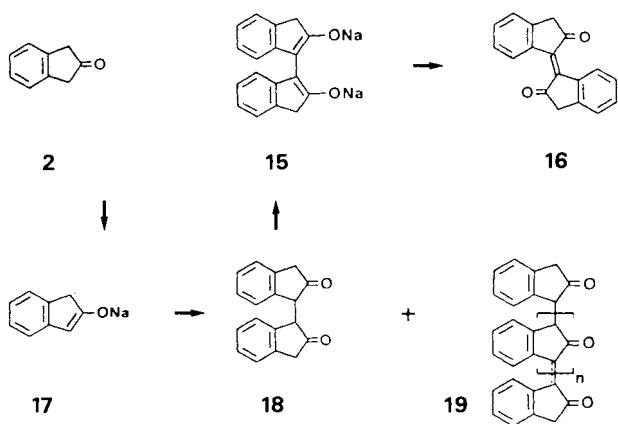
Deprotonation of **13** with NaH (THF) afforded the bis-enolate **11** (see Scheme 1a and Table) which upon quenching with water yielded the diol **10**. Traces of acid converted **10** to its tautomer **13**. Oxidation of **11** with Cu(II) salts produced mixtures of the enediones **14** and **8**⁶⁾. The relative yields of **14** and **8** could be controlled by the temperature

Scheme 1a



of the reaction. Thus, addition of the Cu salt to the THF solution of **11** at -78°C afforded, after recrystallization (from chloroform), **8** in 34% yield. The same procedure at room temperature gave **14** in 43% yield. **8** isomerized to **14** when a small amount of *p*-toluenesulfonic acid was added to its chloroform solution. Similar to the formation of **11**, the diketone **18** could be transformed into the bisenolate **15** (see Scheme 1b and Table). Oxidation of **15** with Cu(II) triflate led to the formation of a single ene-dione **16** (56% yield), in contrast to the oxidation of **11**.

Scheme 1b



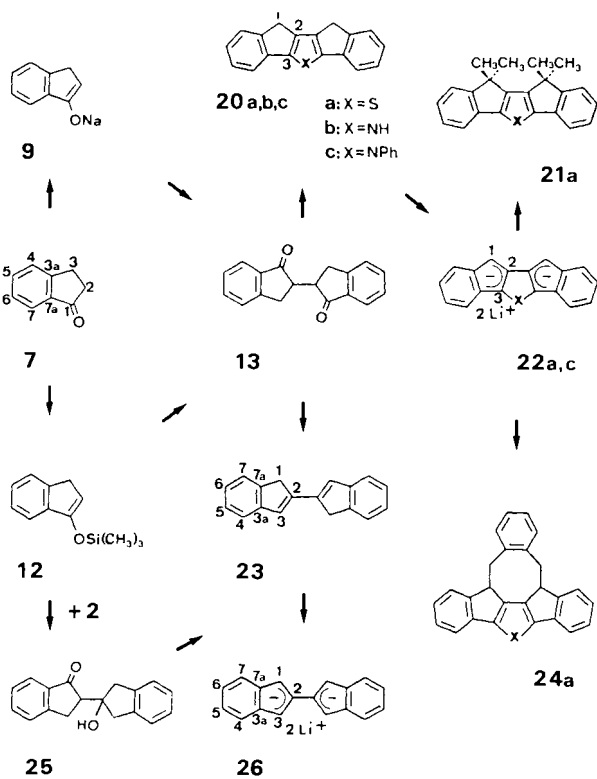
The importance of the diketone **13** as an intermediate for further syntheses is evident from the examples in Scheme 2a. Reduction of **13** with lithium aluminium hydride and treatment of the crude reaction mixture with acetic acid provided access to the known 2,2'-biindenyl **23**⁷⁾ (56%). Ring forming reactions with Lawesson's reagent, ammonia, or aniline produced the thiophene derivative **20a** and the pyrrole species **20b** and **20c**, respectively⁸⁻¹⁴⁾. Compound **13** was converted into **20a** in 90% yield. The oxidation of **7** and the subsequent cyclization of **13** could be performed as

one-pot reactions. For example, the yield of **20a** was 43%, based on **7**. In a similar fashion, the isomeric thiophene **29**^{10,13)} could be prepared from the diketone **18** in 94% yield (see Scheme 2b). Compound **27** served as a model system for the thiophenes **20a** and **29** and was synthesized in 70% yield by treatment of 2-indanone (**2**) with Lawesson's reagent¹⁴⁾.

Regioselective coupling of two indene moieties at the central C-2 positions could also be performed by the crossed aldol addition of the trimethylsilyl enol ether **12** with 2-indanone **2** (see Scheme 2a). The aldol product **25**, thus produced in 45% yield¹⁵⁾, was converted to the known 2,2'-biindenyl **23** by reduction with lithium aluminium hydride and dehydration with acetic acid.

When **20a** was treated with butyllithium (2 equiv.) and quenched with dimethyl sulfate, and when the deprotonation/alkylation sequence was repeated, one obtained **21a** in 63% yield. This finding suggested the intermediacy of the dianion **22a**. Indeed, treatment of **20a**, **c** and **29** in THF with butyllithium at 0°C gave the dianionic species **22a**, **c** and **30**. Thus, the diindenyl-fused heterocycles behave similarly to the biindenyl systems **23** and **27**, which upon analogous treatment with butyllithium were readily transformed into the dianions **26** and **28**, respectively. The structure proof of the dianions relies on both NMR spectroscopy and further quenching experiments. The symmetry inherent in the ¹³C- and ¹H-NMR spectra leaves no doubt that, indeed, a two-fold deprotonation has occurred. Similarly, quenching of **22a** with 1,2-bis(bromomethyl)benzene provided the cyclization product **24** in 46% yield. As expected, the pyrrole

Scheme 2a

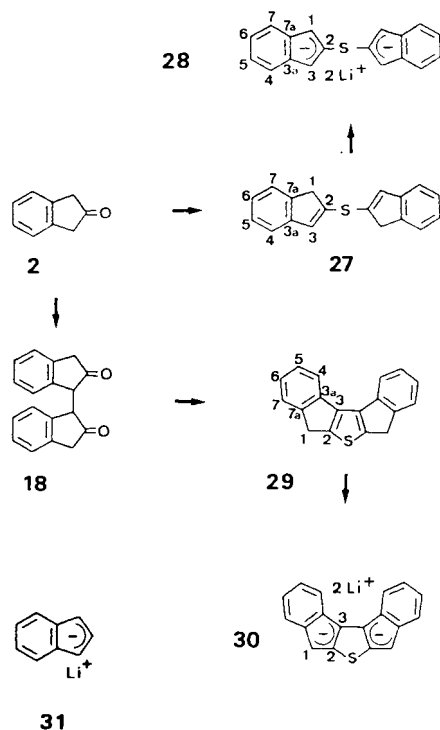


species **20b** could be transformed into a trismetallated derivative, whereby it was advantageous¹⁶⁾ to first remove the N–H proton with sodium hydride and to perform the subsequent deprotonation with butyllithium.

Differentiation between the resonances of tertiary and quaternary C-atoms in the benzene moieties of the enolates **17**, **9**, **11**, and **15** was made utilising spin-echo experiments, the signals of C-4–C-7 and C-3a, C-7a, respectively, were not further assigned. This, however, does not invalidate the arguments given in the discussion based on the average chemical shifts of the benzene moieties.

Spin-echo experiments and the literature data of the parent indenide¹⁷⁾ **31** (see Table) were used to characterize the dianions of the biindenyl derivatives. In the case of non-bridged biindenylides **26** and **28**, we used the relative intensity of the ¹³C-NMR signals to distinguish between the resonances of the quaternary carbons C-3a, C-7a, and C-2. Since carbons C-3a and C-7a are nonequivalent in the bridged diindenylides **22a**, **22c**, and **30**, further assignment of the signals of quaternary carbons was not possible. Therefore, the assignments of the quaternary carbons C-3a, C-7a, and C-2 are only tentative. The most upfield tertiary ¹³C-NMR resonances of the biindenylides were assigned to the deprotonated centres C-1, due to the higher charge density at these positions, in analogy to the case of indenide **31**.

Scheme 2b



2. Discussion

The formation of the hitherto unknown 1,4-diketone **13** by dehydromerization of 1-indanone constitutes an easy way of coupling two indanyl units in the 2-positions. The coupling of **7** can be achieved by quantitative transformation into the enolate and its subsequent oxidation. Alter-

natively, the corresponding silyl enol ether **12**, by treatment of **7** with base and trimethylsilyl chloride, may be subjected to oxidation with lead tetraacetate. The yields obtained from both oxidation techniques are comparable. The intermediate **12** allows for an additional, although non-oxidative method of linking two indanyl moieties at the 2-positions since it brings about a crossed aldol addition between **7** as C–H acidic and **2** as carbonyl component.

The lower yields for **18** in comparison with **13** upon oxidative enolate coupling can readily be attributed to the existence of highly reactive benzylic positions which under the prevailing conditions induce further coupling reactions leading to the formation of the novel oligomer structure **19**. The isolation and structure proof of **19** will be described elsewhere¹⁸⁾.

The importance of these facile coupling reactions is obvious from the further transformations of diketones **18** and **13** which are described in Schemes 1 and 2. The straightforward synthesis of the biindenyl system **23** is an improvement on previous syntheses⁷⁾. The synthetic utility of the diketones **18** and **13** is particularly obvious from the formation of the pyrrole and thiophene species **20a**, **b**, **c** and **29**, the formation of **20a** and **29** can be efficiently performed as a one-pot reaction. The present synthesis of **20a** is clearly superior to the literature procedures which require a great number of steps¹⁰⁾ or give poor yields^{11,12)}. The isomeric dihydrodiindeno[*b,d*]thiophenes **20a** and **29** have recently attracted attention as sulfur containing components of crude oil¹⁹⁾.

The ketones **2** and **7**, the diketones **18** and **13**, and the diindeno-fused heterocycles **20a**, **b**, **c** and **29** and the biindenyls **23** and **27** serve as precursors for organometallic systems with enolate and indenide structures.

The ¹³C-NMR chemical shifts of the enolates **17**, **9** and bisenolates **15**, **11** (see Table) show that the shifts of the "enolate carbons" C-1 in **17**, **15** and C-2 in **9**, **11** are rather similar. However, the delocalization of π -charge into the benzene units is much more pronounced in **9** and **11**. This is deduced from the upfield shift of the average carbon signal of the benzene moieties which is observed in the transition from the ketones to the enolate ions [$\Delta\delta = 10.7$ (**17**), 18.0 (**9**), 8.85 (**15**), 21.3 (**11**)]. The ¹³C-NMR spectra of **17** and **15** indicate that the exchange process of proton transfer between positions C-1 and C-3 is slow on the NMR time scale.

At room temperature, the ¹H- and ¹³C-NMR spectra of **11** ([D₈]THF) exhibit line-broadening effects due to restricted conformational mobility. On cooling to -60°C , each carbon gives rise to three sharp signals of relative intensity 5:5:3. The NMR spectra of the protonated form of the bisenolate **11**, the diol **10**, fail to indicate dynamic behaviour at room temperature.

Treatment of the dihydro systems **23**, **20a**, **20c**, **29**, and **27** with butyllithium in THF gives rise to the stable dianions **26**, **22a**, **22c**, **30**, and **28**. The existence of doubly charged species is clear from the number and position of the ¹³C-NMR signals and from the formation of quenching products such as **24a**. The ¹³C-NMR chemical shifts of C-1 (C-3) and of the aromatic carbons of the dianion **26** are very similar

Table. ^1H - (δ_{H}) and ^{13}C - (δ_{C}) NMR chemical shifts of the anionic species **17**, **9**, **11**, **15**, **22a**, **30**, **26**, **28**, and **31** ($[\text{D}_8]\text{THF}$)^{a)}

	T [°C]	1	3	4–7	2	7a, 3a
$\delta_{\text{C}}(\mathbf{17})^{\text{b)}$	–10	94.3	42.7	126.7, 122.5, 117.8, 114.8	182.2	152.6, 136.0
$\delta_{\text{H}}(\mathbf{17})^{\text{b)}$	–10	5.02	2.98	6.85 (2H), 6.65 (1H), 6.52 (1H)		
$\delta_{\text{C}}(\mathbf{9})$	25	168.1	33.5	125.8, 123.9, 123.7, 117.9	92.2	148.5, 145.7
$\delta_{\text{H}}(\mathbf{9})$	25		3.17	7.50, 7.27, 7.15, 7.05	4.38	
$\delta_{\text{C}}(\mathbf{11})^{\text{c)}$	25	159.5	38.4	126.5, 122.7, 122.5, 116.5	109.5	150.0, 143.3
$\delta_{\text{H}}(\mathbf{11})^{\text{c)}$	25		3.50	7.40–6.30		
$\delta_{\text{C}}(\mathbf{15})$	25	105.9	43.0	126.1, 122.1, 117.7, 117.3	172.8	152.8, 135.9
$\delta_{\text{H}}(\mathbf{15})$	25		3.00	7.00–6.40		
$\delta_{\text{C}}(\mathbf{22a})$	0	78.8	109.5	118.8, 116.2, 113.2, 111.2		(123.1, 133.1, 135.3)
$\delta_{\text{H}}(\mathbf{22a})$	0	6.05		7.25 (4H), 6.38 (4H)		
$\delta_{\text{C}}(\mathbf{30})$	–30	80.5	109.9	(118.9) 117.6 (115.5) 111.8		(133.2, 132.2 [115.5, 118.9])
$\delta_{\text{H}}(\mathbf{30})$	–30	5.88		7.95 (2H), 7.15 (2H), 6.32 (4H)		
$\delta_{\text{C}}(\mathbf{26})$	25		89.8	119.4, 114.9	133.0	131.5
$\delta_{\text{H}}(\mathbf{26})$	25		6.25	7.20 (4H), 6.35 (4H)		
$\delta_{\text{C}}(\mathbf{28})$	25	101.1		123.0, 118.2	130.8	136.5
$\delta_{\text{H}}(\mathbf{28})$	25		5.93	7.06 (4H), 6.32 (4H)		
$\delta_{\text{C}}(\mathbf{31})$			91.7	119.8, 114.4	115.3	129.1

^{a)} ^{13}C -signal assignments are discussed in the text. – ^{b)} **17** has also been measured in $[\text{D}_6]$ dimethyl sulfoxide, see ref.²⁰⁾. – ^{c)} Exchange-broadened signals at room temperature, see text.

to those of the parent indenide **31**¹⁷⁾ (see Table). One concludes that there is no significant redistribution of the π -charge in the biindenylide system **26**. The ion-pair structure of **26** has recently attracted interest²¹⁾ since it is claimed to form "triplet ion pairs" with a twisted arrangement of the separate indenide moieties. The dianions **22a** and **30** should constitute useful model systems for such studies since their indenide units cannot be twisted and the heteroatom provides an additional conjugation path between the separate moieties. The ^{13}C -NMR chemical shifts of the bridged biindenylides **22a**, **22c**, and **30** indicate that there is an unsymmetrical charge-distribution in the allylic subunit (C-1, C-2, C-3) of the dianions with increased electron density at C-1 and decreased electron density at C-3, thus avoiding the formation of antiaromatic thiophene and pyrrole structures. It is important in this context to note the striking difference between the nonbridged biindenylides **26** and **28**. Comparison of charge-induced ^{13}C -signal shifts (see Table and Experimental Part) shows that there is more charge in the carbon skeleton of the parent biindenylide **26** than in that of **28**; obviously, most of the electron density in the diindenylsulfide dianion is located on the sulfur atom. The sulfur bridge of **22a** and **30** enforces a coplanar arrangement of the two indenide moieties, but does not act as a charge acceptor. One concludes, on the other hand, that a strongly twisted arrangement of the separate indenide units is not a requirement for dianion formation. As in the cases of pyrrole and of **20c**, compound **20b** can be transformed into a tris-metallated species which exhibits similar spectroscopic properties to those of **22a** and **22c**.

Studies directed toward further chemical transformations of **18** and **13** are in progress*).

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Experimental

2,2'-Biindenyl-1,1'-dione (13) by Oxidative Coupling of 1-Indanone (7): To a suspension of NaH (2.5 g, 83.3 mmol; 80% oil dispersion) in THF (150 ml) at 25°C under argon was added dropwise (1 h) a solution of **7** (10.0 g, 75.7 mmol) in THF (250 ml). The mixture was stirred at this temperature until there was no further evolution of hydrogen gas, cooled to –78°C, and Cu(II) chloride (11.2 g, 83.3 mmol) was added in one portion. After 0.5 h (stirring), the suspension was warmed to room temperature and after another 0.5 h (stirring) quenched with water (40 ml). THF was removed under reduced pressure, and the residue was dissolved in ether, washed with water, dried (MgSO_4), and concentrated to give a crude product, which was recrystallized from methanol to yield **13** (5.0 g, 50%), (*meso/d,l* mixture), mp 140°C. – ^1H NMR: δ = 7.75–7.35 (m, arom. H); 3.50–3.20, 2.95–2.45 (m, 2-H, 3-H). – ^{13}C NMR: δ = 207.0, 205.9 (CO); 153.6, 153.2, 136.89, 136.86 (quat. C); 134.9, 134.6, 127.5, 127.4, 126.6, 126.4, 123.9, 123.8 (arom. C); 48.2, 47.0 (C-2); 30.8, 28.2 (C-3). – IR (KBr): $\nu(\text{CO})$ = 1700 cm^{-1} .

$\text{C}_{18}\text{H}_{14}\text{O}_2$ (262.3) Calcd. C 82.48 H 5.38
Found C 82.32 H 5.40

1,1'-Biindenyl-2,2'-dione (18) by Oxidative Coupling of 2-Indanone (2): To a suspension of NaH (1.5 g, 50.0 mmol) in THF (75 ml) at 0°C under argon was added dropwise (1 h) a solution of **2** (6.0 g, 45.5 mmol) in THF (75 ml). After stirring for 10 min at 0°C, the ice bath was removed, and the mixture was stirred for 10 min. The solution of **17** was transferred into a dropping funnel at –78°C and added dropwise (3 h) to a stirred suspension of Cu(II) triflate (18.08 g, 50.0 mmol) in THF (75 ml) at –78°C. After 1 h, the suspension was quenched with THF/water (30 ml) at –78°C and allowed to warm to room temperature. THF was removed under reduced pressure, and the residue was dissolved in ether, washed with water, dried (MgSO_4), and concentrated. Chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as eluant gave **18** (1.8 g, 30%), (*meso/d,l* mixture), mp 168°C (decomp.). – ^1H NMR: *meso* isomer, δ = 7.28 (m, 4H, arom. H), 7.15 (m, 2H, arom. H),

* Note added in proof: Another short synthesis of **20a** and **29** from **7** has just been described: C.-D. Czogalla, F. Boberg, *Phosphorus Sulfur* **35** (1988) 127.

6.85 (d, 2H, arom. H); 4.22 (s, 2H, 1-H); 3.52, 3.38 (AB, 4H, 3-H); *d,l* isomer, $\delta = 7.21$ (d, 2H, arom. H), 7.11 (t, 2H, arom. H), 7.01 (t, 2H, arom. H), 6.75 (d, 2H, arom. H); 4.40 (s, 2H, 1-H); 3.70, 3.53 (AB, 4H, 3-H). — ^{13}C NMR: *meso* isomer, $\delta = 214.9$ (CO); 139.1, 138.1 (quat. C); 128.1, 127.6, 125.2, 124.1 (arom. C); 55.3 (C-1); 43.3 (C-3); *d,l* isomer, $\delta = 216.0$ (CO); 138.1, 136.8 (quat. C); 127.8, 127.4, 125.0, 124.2 (arom. C); 54.4 (C-1); 43.6 (C-2, 3). — IR (KBr): $\nu(\text{CO}) = 1730, 1700 \text{ cm}^{-1}$.

$\text{C}_{18}\text{H}_{14}\text{O}_2$ (262.3) Calcd. C 82.48 H 5.38
Found C 82.21 H 5.40

In a procedure analogous to that described for the preparation of **13** from **7**, only 0.9 g (15%) of **18** was obtained. Extensive variation of the experimental conditions (e.g. diethyl ether as solvent, iodine as oxidizing reagent and LDA, LiNH_2 or KNH_2 as base) did not improve the yield of **18**.

Paal-Knorr Synthesis of 20b from 13 and NH_3 : To absolute ethanol (50 ml), saturated with ammonia gas (dried over potassium) under ice cooling, was added **13** (1.0 g, 3.82 mmol) and *p*-toluenesulfonic acid (20 mg), and the mixture was heated (stirring) in a sealed pressure vessel for 18 h at 200 °C. After cooling, the solvent was removed under reduced pressure and the residue recrystallized from toluene (saturated with argon) to give **20b** (550 mg, 59%), mp 275 °C (decomp.). — ^1H NMR: $\delta = 11.8$ (s, NH); 7.5–6.9 (m, arom. H); 3.4 (s, 3-H). — ^{13}C NMR: $\delta = 145.8, 141.1, 135.8$ (quat. C); 126.5, 125.1 (arom. C); 123.5 (quat. C); 122.6, 115.7 (arom. C); 29.6 (C-3). — IR (KBr): $\nu(\text{NH}) = 3390 \text{ cm}^{-1}$.

$\text{C}_{18}\text{H}_{13}\text{N}$ (243.3) Calcd. C 88.86 H 5.39 N 5.75
Found C 88.31 H 5.13 N 5.75

Deprotonation of 20a and Alkylation of the Corresponding Dianion 22a with 1,2-Bis(bromomethyl)benzene (Synthesis of 24a): To a suspension of **20a** (0.5 g, 1.92 mmol) in THF (50 ml) at 0 °C under argon was added dropwise 3.25 ml (4.23 mmol) of BuLi (1.3 M in hexane). After stirring for 15 min at 0 °C, the red solution of the dianion **22a** was cooled to –78 °C, and 1,2-bis(bromomethyl)benzene (0.61 g, 2.31 mmol), dissolved in THF (40 ml), was added dropwise (0.5 h). The mixture was stirred for another 2 h at –78 °C, 1.5 h at 0 °C and then left at room temperature for about 12 h. The solution was quenched with saturated ammonium chloride solution, extracted with toluene, washed with water, dried (MgSO_4), and concentrated. Chromatography of the crude product (silica gel, toluene) yielded **24a** (314 mg, 45%), mp 260 °C (decomp.). — ^1H NMR: $\delta = 7.62$ (d, 2H, arom. H); 7.54 (m, 2H, arom. H); 7.44 (d, 2H, arom. H); 7.34 (m, 4H, arom. H); 7.25 (m, 2H, arom. H); 3.84 (d, 2 × CH); 3.34, 2.85 (AB, 2 × CH₂). — ^{13}C NMR: $\delta = 149.4, 148.1, 145.2, 140.8, 139.2$ (quat. C); 131.6, 127.5 (2C); 125.0, 124.2, 118.5 (arom. C); 50.1 (2 × CH); 38.1 (2 × CH₂).

$\text{C}_{26}\text{H}_{18}\text{S}$ (362.5) Calcd. C 86.15 H 5.01 S 8.85
Found C 86.32 H 4.85 S 8.50

2,2'-Biindanyl-1,1'-dione (13) by Oxidative Coupling of 3-Trimethylsilyloxy-1H-indene (12): To a stirred solution of **12** (1.02 g, 5 mmol) in dry methylene chloride (5 ml) at –78 °C under argon lead tetraacetate (1.1 g, 2.5 mmol) was added in one portion, and subsequently the suspension was treated with THF (5 ml) in order to dissolve $\text{Pb}(\text{OAc})_4$. The reaction mixture was stirred for 1.5 h at –78 °C, then allowed to warm slowly to room temperature and stirred for another hour at this temperature. The solution was quenched with water (10 ml), extracted with ether and concentrated to give a residue, which was recrystallized from ethanol to give **13** (210 mg, 32%).

Hydroxy Ketone 25 by Crossed Aldol Addition of 3-Trimethylsilyloxy-1H-indene (12) with 2-Indanone (2): To a stirred mixture of **2**

(1.45 g, 11 mmol) and TiCl_4 (2.2 g, 11 mmol) in dry CH_2Cl_2 (40 ml) at room temperature under argon was added dropwise a solution of **12** (2.04 g, 10 mmol) in dry CH_2Cl_2 (40 ml), and the mixture was stirred for 4 h. After quenching with water (40 ml), the resulting organic layer was extracted with ether, the combined extracts were washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue washed for 3 times with hexane (30 ml). Recrystallization from ethanol gave **25** (1.2 g, 45%), mp 139.5–140 °C. — ^1H NMR: $\delta = 7.81$ –7.13 (m, 8H, arom. H); 3.96 (s, br., 1H, OH); 3.37–3.26 (m, 6H, benz. H), 3.18–3.12 (2 d, 1H, 2-H), 3.01–2.91 (m, 6H, benz. H). — ^{13}C NMR: $\delta = 208.7$ (CO); 153.8, 140.9, 140.6, 137.1 (quat. C); 135.2, 127.5, 126.7, 126.6, 126.5, 124.8, 123.9 (arom. C); 82.6, 54.7 (C-2); 46.2 (C-1); 44.1, 30.0 (C-3). — IR (KBr): $\nu(\text{CO}) = 1683 \text{ cm}^{-1}$.

$\text{C}_{18}\text{H}_{16}\text{O}_2$ (264.3) Calcd. C 81.79 H 6.10
Found C 81.76 H 6.02

2,2'-Biindenyl (23): To a suspension of LiAlH_4 (0.87 g, 22.9 mmol) in THF (30 ml) was added dropwise a solution of **13** (1.0 g, 3.82 mmol) in THF (30 ml) and the mixture stirred at room temperature for about 12 h. Water was added, the solution acidified with aqueous sulfuric acid, and the aqueous layer extracted with ether. After drying (MgSO_4), the solvent was removed under reduced pressure and the crude reaction product treated (under argon) for about 12 h with acetic acid (100 ml). A few crystals of hydroquinone were added at room temperature. To isolate **8**, the solution was extracted with chloroform and the combined organic layers washed exhaustively with water to remove acetic acid. After drying (MgSO_4), the solvent was removed under reduced pressure and the residue recrystallized from toluene to give **23** (490 mg, 56%), mp 238 °C (decomp.). — ^1H NMR: $\delta = 7.30$ (m, 8H, arom. H); 6.93 (s, 2H, olefin. H); 3.73 (s, 4H, CH₂). — ^{13}C NMR: $\delta = 145.4, 143.5, 143.0$ (quat. C); 128.0, 126.7, 125.0, 123.7, 120.9 (arom./olefin. C); 38.7 (CH₂).

Oxidation of the Biindanones 13 and 18 to the Ene-diones 14, 8, 16: To a stirred suspension of NaH (92 mg, 4.8 mmol; 80% oil dispersion) in THF (25 ml) at 0 °C under argon was added dropwise (0.5 h) a solution of the dione (500 mg, 1.9 mmol) in THF (50 ml). After 15 minutes, the mixture was cooled to –78 °C and $\text{Cu}(\text{OTf})_2$ (1.73 g, 4.8 mmol) was added in one portion. After 1 h (stirring), the suspension was warmed to room temperature and after 0.5 h (stirring) quenched with water (10 ml). THF was removed under reduced pressure and the aqueous layer was extracted (three times) with chloroform. The combined organic extracts were washed with water, dried (MgSO_4), and concentrated to give a crude product which was recrystallized from methanol to yield **8** (170 mg, 34%), mp 200 °C (decomp.). The same procedure at room temperature gave **14** (210 mg, 43%), mp 225 °C (decomp.).

16: Filtration of the crude product (silica gel, hexane/ethyl acetate (5:1) and recrystallization (methanol) yielded **16** (220 mg, 55%), mp 163 °C (decomp.).

14: ^1H NMR: $\delta = 7.86$ (d, 2H, arom. H); 7.63 (t, 2H, arom. H); 7.58 (d, 2H, arom. H); 7.41 (t, 2H, arom. H); 4.32 (s, 4H, CH₂). — ^{13}C NMR: $\delta = 196.8$ (CO); 151.0, 138.3 (quat. C); 135.4 (quat. C); 127.6, 126.6, 124.1 (arom. C); 32.4 (CH₂). — IR (KBr): $\nu(\text{CO}) = 1670 \text{ cm}^{-1}$.

$\text{C}_{18}\text{H}_{12}\text{O}_2$ (260.3) Calcd. C 83.06 H 4.65
Found C 82.23 H 4.72

8: ^1H NMR: $\delta = 7.83$ (d, 2H, arom. H); 7.58 (t, 2H, arom. H); 7.46 (d, 2H, arom. H); 7.37 (t, 2H, arom. H); 3.82 (s, 4H, CH₂). — ^{13}C NMR: $\delta = 189.0$ (CO); 146.8, 142.5, 139.6 (quat. C); 134.7, 127.9, 125.9, 125.0 (arom. C); 34.0 (CH₂).

$\text{C}_{18}\text{H}_{12}\text{O}_2$ (260.3) Calcd. C 83.06 H 4.65
Found C 82.97 H 4.72

16: $^1\text{H NMR}$: δ = 8.63 (m, 2H, arom. H, *ortho*); 7.38 (m, 6H, arom. H); 3.64 (s, 4H, 3,3'-H). — $^{13}\text{C NMR}$: δ = 203.8 (CO); 139.6, 139.1, 137.4 (quat. C); 131.4, 129.2, 126.9, 124.5 (arom. C); 42.8 (C-3,3'). — IR (KBr): $\nu(\text{CO}) = 1705 \text{ cm}^{-1}$.

$\text{C}_{18}\text{H}_{12}\text{O}_2$ (260.3) Calcd. C 83.06 H 4.65
Found C 82.98 H 4.59

Paal-Knorr Synthesis of 20c from 13 and Aniline: A solution of **13** (1.0 g, 3.8 mmol), aniline (0.34 g, 3.6 mmol), and *p*-toluenesulfonic acid (20 mg) in toluene (25 ml) was heated at reflux for 15 h. The mixture was concentrated and the residue dissolved in petroleum ether; the organic layer was washed with water and dried (MgSO_4). Solvent removal and chromatography on silica gel (petroleum ether/ethyl acetate, 10:1) gave **20c** (0.4 g, 35%), mp 169°C. — $^1\text{H NMR}$: δ = 7.70–7.40 (m, 7H, arom. H), 7.20–6.95 (m, 6H, arom. H); 3.60 (s, 4H, CH_2). — $^{13}\text{C NMR}$: δ = 146.6, 142.4, 138.8, 135.7, 129.4, 127.9, 126.6, 126.3, 125.3, 125.1, 123.2, 116.5, 30.1.

$\text{C}_{24}\text{H}_{17}\text{N}$ (319.4) Calcd. C 90.25 H 5.36 N 4.38
Found C 90.38 H 5.36 N 4.47

Cyclization of the Biindanones 13 and 18 to the Corresponding Thiophenes 20a and 29. — **20a:** A solution of **13** (3.6 g, 13.7 mmol) and Lawesson's reagent [2,4-Bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide] (6.7 g, 16.3 mmol) in toluene (100 ml) was heated at reflux for 2.5 h. Toluene was removed under reduced pressure and the residue recrystallized from chloroform to give **20a** (3.2 g, 90%), mp 288°C. — $^{13}\text{C NMR}$: δ = 145.8, 145.5, 141.6, 139.7 (quat. C); 127.0, 125.1, 124.6, 118.4 (arom. C); 33.3 (2 \times CH_2).

29: Using a procedure analogous to that for **20a**, **18** (1.5 g, 5.7 mmol) and Lawesson's reagent (2.8 g, 6.8 mmol) in toluene (150 ml) gave a crude product which was chromatographed (silica gel, petroleum ether/ethyl acetate, 5:1) to give **29** (1.4 g, 94%), mp 216°C. — $^{13}\text{C NMR}$: δ = 147.7, 146.4, 139.7, 139.2 (quat. C); 126.8, 124.8, 124.3, 120.6 (arom. C); 35.2 (2 \times CH_2).

Di(2-indenyl) Sulfide (27): 2-Indanone (**2**) (3.0 g, 22.7 mmol) and Lawesson's reagent (5.45 g, 13.3 mmol) in toluene (40 ml) were heated under reflux for 2.5 h. After about 12 h of stirring at room temperature, toluene was removed under reduced pressure and the residue chromatographed (silica gel, petroleum ether/ethyl acetate, 5:1) to give **27** (2.1 g, 70%), mp 96°C. — $^1\text{H NMR}$: δ = 7.42 (d, 2H, arom. H), 7.30 (m, 4H, arom. H), 7.20 (m, 2H, arom. H), 6.93 (s, 2H, 1-H), 3.60 (s, 4H, 3-H). — $^{13}\text{C NMR}$: δ = 144.4, 143.4, 139.9, (quat. C), 133.1, 126.7, 124.7, 123.4, 120.3 (arom. C), 42.6 (C-3).

$\text{C}_{18}\text{H}_{14}\text{S}$ (262.4) Calcd. C 82.40 H 5.38 S 12.22
Found C 82.29 H 5.40 S 11.98

10,10,11,11-Tetramethyl-10H,11H-diindenol[1,2-b:2',1'-d]thiophene (21a) by Permethylolation of 20a: To a suspension of **20a** (0.5 g, 1.92 mmol) in THF (100 ml) at 0°C under argon was added dropwise 3.25 ml (4.23 mmol) of BuLi (1.3 M in hexane). After additional 15 min, the red dianion solution was quenched with dimethyl sulfate (0.53 g, 4.23 mmol) and the resultant dark green mixture was stirred for another 2 h at 0°C. This procedure (BuLi/DMS) was alternately repeated for three times. The solution was allowed to reach room temperature and after 0.5 h (stirring) quenched with water and extracted with petroleum ether. The combined organic extracts were washed with water, dried (MgSO_4), and evaporated

to give a crude product, which was chromatographed (silica gel, petroleum ether/ethyl acetate, 5:1) to give **21a** (385 mg, 63%). Further purification was achieved by recrystallization from ethanol, mp 192°C. — $^1\text{H NMR}$: δ = 7.36 (2 d, 4H, arom. H), 7.26 (t, 2H, arom. H), 7.18 (t, 2H, arom. H), 1.65 (s, 12H, CH_3). — $^{13}\text{C NMR}$: δ = 155.7, 152.1, 143.3, 137.0 (quat. C), 127.0, 125.2, 121.9, 118.2, (arom. C), 46.3 (quat. C), 26.7 (CH_3).

$\text{C}_{22}\text{H}_{20}\text{S}$ (316.5) Calcd. C 83.50 H 6.37 S 10.13
Found C 83.53 H 6.40 S 10.07

CAS Registry Numbers

7: 83-33-0 / (*Z*)-**8:** 115679-38-4 / **9** · Na^+ : 107402-28-8 / 11^2 · 2 Na^+ : 115679-39-5 / **12:** 31928-64-0 / (\pm)-**13** (isomer 1): 115679-35-1 / **13** (isomer 2): 115679-40-8 / (*E*)-**14:** 115679-41-9 / 15^2 · 2 Na^+ : 115679-42-0 / (*E*)-**16:** 115679-43-1 / **17** · Na^+ : 115679-44-2 / **18** (isomer 1): 115679-45-3 / (\pm)-**18** (isomer 2): 115679-36-2 / **20a:** 7099-33-4 / **20b:** 7099-31-2 / **20c:** 115679-37-3 / **21a:** 115679-46-4 / **22a:** 115705-12-9 / **23:** 787-61-1 / **24a:** 115679-47-5 / **25:** 115679-48-6 / **26:** 115679-49-7 / **27:** 115679-50-0 / **28:** 115679-51-1 / **29:** 7099-34-5 / **30:** 115679-53-3 / **31:** 20669-47-0 / *o*-(BrCH_2) C_6H_4 : 91-13-4 / PhNH_2 : 62-53-3 / 2-indanone: 615-13-4

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[151/88]